Synthesis of Seven-Membered Cyclic Enol Ether Derivatives from the Reaction of a Cyclic Phosphonium Ylide with α,β-Unsaturated Esters

Tetsuya Fujimoto,* Yoh-ichi Kodama, and Iwao Yamamoto

Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Tokida, Ueda 386, Japan

Akikazu Kakehi

Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380, Japan

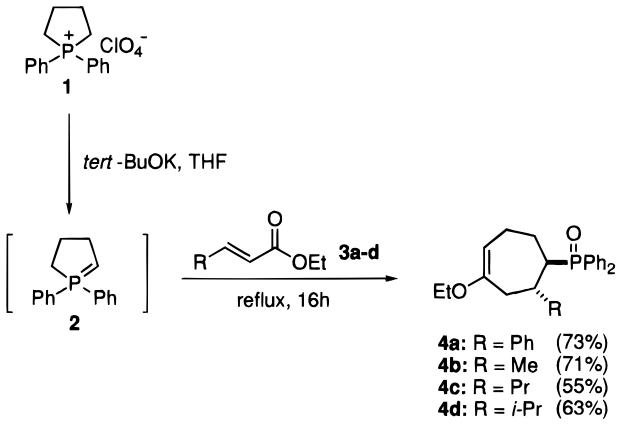
Received April 28, 1997[⊗]

The tandem Michael−intramolecular Wittig reactions of a five-membered cyclic phosphonium ylide (**2**) with α,β-unsaturated esters afforded seven-membered cyclic enol ether derivatives **4a**−**e** in 37−73% yield. The reaction proceeded via a rigid phosphabicyclic intermediate and supplied the enol ether derivatives with high stereoselectivity. On the other hand, the reaction using ethyl acrylate as a substrate gave the 1:3 adduct **15** of the ylide and the enoate via the repetition of the Michael-type addition and regeneration of the ylide followed by the intramolecular Wittig reaction.

The reaction of a cyclic phosphonium ylide with enones provided cycloheptene and hydroazulene derivatives with high stereoselectivity by tandem Michael−intramolecular Wittig reactions via a rigid phosphabicycle or phosphatricycle.[1,2] In this work, we attempted to examine the reaction using α,β-unsaturated esters instead of enones in order to increase the versatility of this reaction.

The reaction of a cyclic phosphonium ylide (**2**), generated from the corresponding salt **1** using *t*-BuOK as a base, with ethyl cinnamate (**3a**) was carried out under the same reaction conditions as previously reported.[1] Consequently, it wsa clarified that a seven-membered cyclic enol ether derivative (**4a**), which would be considered to be formed via the same reaction course as using enones, was obtained in 73% yield (Scheme 1). Although most of the reactions of phosphonium ylides with enoates were thus far employed for the sake of cyclopropane synthesis,[3] the product that stemmed from the addition−elimination reaction was not detected from the reaction of **2** with enoate **3a**. In the intramolecular Wittig reaction of the regenerated ylide with ester functionality after the Michael-type addition of **2** to **3a**, the reaction between a nonstabilized ylide and nonactivated ester was involved. In general, the reaction of nonstabilized phosphonium ylides with esters, whether intramolecular[4] or intermolecular,[5] was reported to lead to acylation of the ylides followed by generation of stable β-keto phosphonium ylides. The formation of enol ethers by the reaction of phosphonium ylides with esters was reported to be

Scheme 1



favorable in the case of the reaction using stabilized or semistabilized phosphonium ylides[6] or employing a fluoroalkanoate as a substrate.[7] The fact that the present reaction predominantly gave the enol ether **4a** would be attributed to the formation of a more preferable syn ethoxy betaine intermediate than its anti adduct which would lead to a keto phosphonium salt,[7a] because of the 1,3-diaxial interaction between the ethoxy group and phenyl group attached to the phosphorus atom. Moreover, regeneration of a stable keto phosphonium ylide from the phosphabicyclic keto phosphonium salt is difficult, because an acidic proton is attached to a bridgehead carbon atom, which would also prevent the intramolecular acylation of the regenerated phosphonium

[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1997.

(1) Fujimoto, T.; Takeuchi, Y.; Kai, K.; Hotei, Y.; Ohta, K.; Yamamoto, I. *J. Chem. Soc., Chem. Commun.* **1992**, 1263−1264.

(2) Fujimoto, T; Uchiyama, Y.; Kodama, Y.; Ohta, K.; Yamamoto, I.; Kakehi, A. *J. Org. Chem.* **1993**, *58*, 7322−7323.

(3) (a) Bernardi, A.; Scolastico, C.; Villa, R. *Tetrahedron Lett.* **1989**, *30*, 3733−3734. (b) Mulzer, J.; Kappert, M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 63−64. (c) Devos, M. J.; Hevesi, L.; Bayet, P.; Krief, A. *Tetrahedron Lett.* **1976**, 3911−3914. (d) Dauben, W. G.; Kozikowski, A. P. *Tetrahedron Lett.* **1973**, 3711−3714. (e) Grieco, P. A.; Finkelhor, R. S. *Tetrahedron Lett.* **1972**, 3781−3783. (f) Bestmann, H. J.; Seng, F. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 116−117.

(4) (a) Bergelson, L. D.; Shemyakin, M. M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 250−260. (b) House, H. O.; Babad, H. *J. Org. Chem.* **1963**, *28*, 90−92.

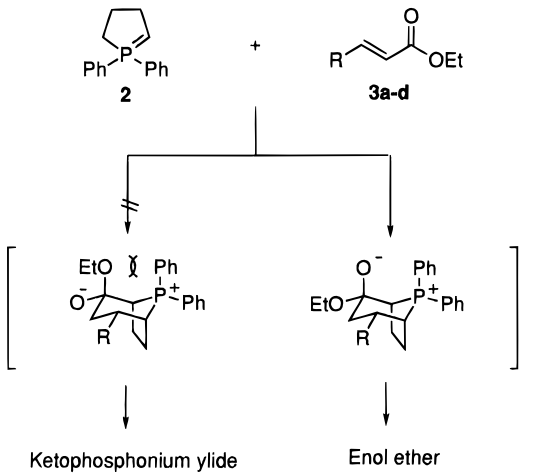
(5) (a) Trippett, S.; Walker, D. M. *J. Chem. Soc.* **1961**, 1266−1272. (b) Wittig, G.; Schöllkopf, U. *Chem. Ber.* **1954**, *87*, 1318−1330.

(6) (a) Aitken, R. A.; Thom, G. L. *Synthesis* **1989**, 958−959. (b) Murphy, P. J.; Brennan, J. *Chem. Soc. Rev.* **1988**, *17*, 1−30. (c) Brennan, J.; Murphy, P. J. *Tetrahedron Lett.* **1988**, *29*, 2063−2066. (d) Hercouet, A.; Le Corre, M. *Tetrahedron* **1981**, *37*, 2867−2873. (e) Hercouet, A.; Le Corre, M. *Tetrahedron Lett.* **1979**, 2995−2998. (f) Subramanyam, V.; Silver, E. H.; Soloway, A. H. *J. Org. Chem.* **1976**, *41*, 1272−1273. (g) Dauben, W. G.; Hart, D. J. *Tetrahedron Lett.* **1975**, 4353−4356. (h) Texier, F.; Carrié, R. *Tetrahedron Lett.* **1971**, 4163−4166. (i) Ploder, W. H.; Tavares, D. F. *Can. J. Chem.* **1970**, *48*, 2446−2448.

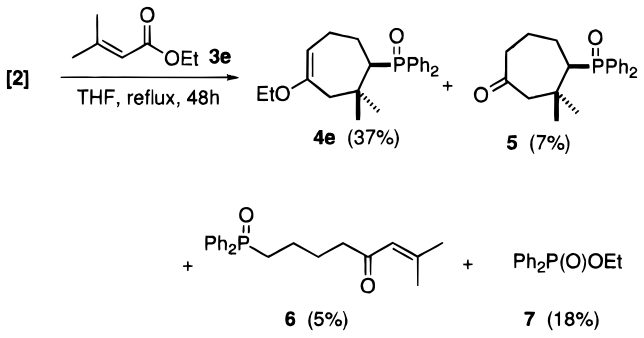
(7) (a) Bégué, J. P.; Bonnet-Delpon, D.; Mesureur, D.; Née, G.; Wu, S. W. *J. Org. Chem.* **1992**, *57*, 3807−3814. (b) Bestmann, H. J.; Dornauer, H.; Rostock, K. *Chem. Ber.* **1970**, *103*, 2011−2015. (c) Bestmann, H. J.; Rostock, K.; Dornauer, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 308.

S0022-3263(97)00751-2 CCC: $14.00

Scheme 2



Scheme 3



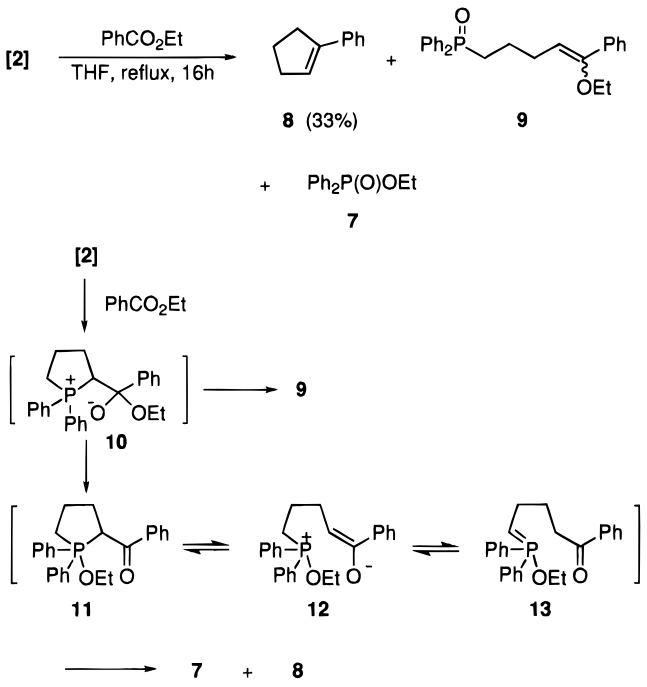
ylide (Scheme 2). The presence of Li salts was reported to be favorable for acylation,[7a] but even though *n*-BuLi was employed as a base, **4a** was obtained in 16% yield. The reaction of **2** with enoates **3b**−**d** also afforded the corresponding enol ether derivatives **4b**−**d** in 55−71% yields (Scheme 1).

On the other hand, the reaction of **2** with 3,3-dimethylacrylate (**3e**) provided ketone **5**, oxoalkenylphosphine oxide **6**, and ethyl diphenylphosphinate (**7**) as well as the corresponding enol ether **4e** (Scheme 3). Ketone **5** was thought to be supplied by hydrolysis of part of the initial product **4e**, and phosphine oxide **6** was assumed to be formed via the Wittig reaction of **2** with **3e** followed by hydrolysis of the resulting acyclic enol ether.

The formation of **4e** and **5** was an unexpected result because the reaction using mesityl oxide having a structure analogous to 3,3-dimethylacrylate did not give a Michael−Wittig product but a Wittig product.[1] These results suggested that the reaction path of the cyclic phosphonium ylide **2** with α,β-unsaturated carbonyl compounds is determined by the first nucleophilic attack of the ylide **2** rather than the transition state during the intramolecular Wittig reaction as we considered in the previous paper.[1] For the reaction of 3,3-dimethylacrylate, both reactions initiated by the 1,2- and 1,4-addition of the ylide **2** to the enoate **3e** would competitively proceed to afford a mixture of **4e**, **5**, and **6**.

On the other hand, ethyl diphenylphosphinate (**7**) was assumed to be formed from the reaction initiated by the 1,2-addition of the ylide **2** to the enoate **3e**, because **7** was not obtained from the reaction using the other acrylate derivatives **3a**−**d** which were monosubstituted on the β-carbon atom. In order to clarify the mechanism for yielding **7**, the reaction of **2** with ethyl benzoate was

Scheme 4

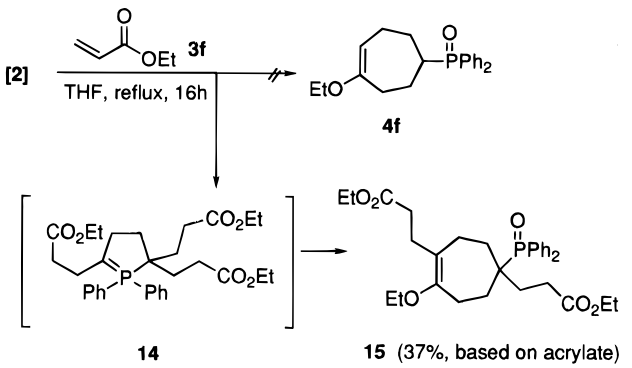


attempted (Scheme 4). The reaction of **2** with ethyl benzoate under refluxing conditions for 16 h using THF as a solvent afforded 1-phenylcyclopentene (**8**), alkenylphosphine oxide **9** (as a mixture of **7**), and ethyl diphenylphosphinate (**7**). The product **8** was thought to be obtained along with **7** from the intramolecular Wittig reaction of the alkoxyphosphonium ylide **13** which would be generated from an intramolecular rearrangement of the ethoxy group into the phosphorus atom in an initial intermediate (**10**) followed by regeneration of the phosphonium ylide via betaine **12**. Uijttewaal et al.[8] determined the same rearrangement of the alkoxy group in the reaction of an excess amount of methylenetriphenylphosphorane with esters and reported the synthesis of branched olefins via nucleophilic attack on the alkoxy group in the resulting pentacoordinate phosphorus intermediate. For the present reaction, the corresponding pentacoordinate intermediate **11** would lead to **7** and **8** without losing the ethoxy group because of using an equimolar amount of the starting phosphonium ylide **2** and/or because the betaine **12** was capable of changing into the alkoxyphosphonium ylide **13** leading to the intramolecular Wittig product **8**. The formation of **7** during the reaction of **2** with 3,3-dimethylacrylate (**3e**) could be explained by postulating the same reaction course. Although the existence of the corresponding cyclopentene derivative was intimated on TLC, attempts to isolate it were unsuccessful because it changed into a more polar one. Alkenylphosphine oxide **9** would be competitively formed from the alkoxy betaine intermediate **10**. Although it was suggested from the ^{13}C NMR spectrum that the phosphine oxide **9** was stereoselectively obtained, its geometry was not determined.

Finally, the reaction of ethyl acrylate (**3f**) with **2** was carried out under the same reaction conditions as for **3a**−**d** (Scheme 5). Consequently, the 1:3 adduct **15** of the phosphonium ylide **2** and acrylate **3f** was isolated in

(8) (a) Uijttewaal, A. P.; Jonkers, F. L.; Van der Gen, A. *J. Org. Chem.***1979**, *44*, 3157−3168. (b) Uijttewaal, A. P.; Jonkers, F. L.; Van der Gen, A. *J. Org. Chem.* **1978**, *43*, 3306−3311. (c) Uijttewaal, A. P.; Jonkers, F. L.; Van der Gen, A. *Tetrahedron Lett.* **1975**, 1439−1442.

Scheme 5



37% yield (based on the acrylate) instead of a normal Michael−intramolecular Wittig product **4f**. The structure of the adduct was assigned to **15** on the basis of the ^{1}H NMR, ^{13}C NMR, and mass spectra. The adduct **15** was thought to be supplied from the intramolecular Wittig reaction of an intermediate (**14**) which would be generated by the repetition of the Michael addition of **2** to **3f** and regeneration of the ylide. The Michael addition of the cyclic phosphonium ylide to ethyl acrylate (**3f**) would be faster than the intramolecular Wittig reaction until the formation of the intermediate **14**. The intramolecular Wittig reaction from **14** giving **15** would then be preferable to the addition due to the sterically crowded circumstances around the ylide carbon atom in **14**.

The enol ether derivatives **4a**−**d** obtained from these reactions were single products because in these ^{13}C NMR spectra peaks ascribed to other stereoisomers were not detected (Table 1). However, the stereochemistry relevant to the cis or trans configuration of two substituents bonded to the cycloheptene ring was not determined because all of them were gradually hydrolyzed and changed into the corresponding ketones at room temperature. Also, the stereochemistry was not clarified by NOE measurements due to the flexibility of the cycloheptene skeleton. However, comparison of the ^{13}C NMR for **4a** with the previously reported cycloheptene derivative **16**[1] which was later confirmed to have a *trans* relationship on the basis of X-ray crystallography[9] suggested that **4a** has an analogous ring conformation and a similar dihedral angle between the $Ph_2P(O)$ and Ph groups to **16**. The sp^3 carbon atoms of the cycloheptene ring had almost similar chemical shifts and coupling constants (J_{PC}) to them in **16**. Also, each ipso carbon atom of the phenyl group adjacent to the $Ph_2P(O)$ group of **4a** and **16** was observed as a couple of doublet peaks which had almost the same chemical shift and coupling constant, 145.4 ppm (4.3 Hz) for **4a** and 145.6 ppm (3.4 Hz) for **16**. Moreover, the intramolecular Wittig reaction was considered to proceed via a similar rigid phosphabicycle for the reaction using acyclic and cyclic enones.[1,2] Accordingly, it was also suggested from the reaction mechanism that *trans* enol ether derivatives were predominantly formed.

In conclusion, the reaction of the cyclic phosphonium ylide **2** with enoates provided the seven-membered cyclic enol ether derivatives with high stereoselectivity via the tandem Michael−intramolecular Wittig reaction. In addition, a novel reaction course was determined for the reaction using ethyl acrylate and ethyl benzoate.

(9) Unpublished data.

Experimental Section

General Procedures. Reactions were run in dried glassware under a nitrogen atmosphere. THF was distilled from sodium benzophenone ketyl prior to use. Flash column chromatography was carried out on silica gel (Wakogel C-300). Ethyl 2-hexenoate (**3c**) and ethyl 4-methyl-2-pentenoate (**3d**) were prepared from triethyl phosphonoacetate and the corresponding aldehyde by the method of Marmor.[10] 1,1-Diphenylphospholanium perchlorate (**1**) was prepared by the reaction of tetraphenyldiphosphine with 1,4-dibromobutane[11] followed by exchange of Br^- into ClO_4^- with a saturated aqueous $NaClO_4$ solution. All other reagents were available from commercial sources and were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were acquired on a 90 MHz spectrometer using $CDCl_3$ as the solvent. Chemical shifts are reported in δ from TMS as the internal standard. Mass spectra and HRMS were obtained using EI ionization at 70 eV. Melting points are uncorrected.

General Procedure of the Reaction of Cyclic Phosphonium Ylide 2 with Enoates 3a−e. A solution of phosphonium salt (2.00 g, 5.87 mmol) and potassium *tert*-butoxide (0.66 g, 5.87 mmol) in dry THF (25 mL) was stirred at room temperature for 1 h. A solution of enoates (5.87 mmol) in dry THF (5 mL) was added dropwise to the mixture, and the resulting solution was refluxed for 16 h (48 h for **4e**). After being cooled to room temperature, the mixture was quenched with water and extracted with CH_2Cl_2 or $CHCl_3$. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using AcOEt−$CHCl_3$ (1/1) as an eluent.

***trans*-(4-Ethoxy-2-phenyl-4-cyclohepten-1-yl)diphenylphosphine oxide (4a)**: 1.79 g (73%); white solid, mp 170−174 °C; ^{1}H NMR δ 1.09 (t, J = 7 Hz, 3H), 2.01−3.62 (m, 10H), 4.57 (brt, 1H), 6.94−7.89 (m, 15H); IR (KBr) 1655 (C=C), 1160 cm^{-1} (P=O); MS m/z 416 (M^+). Anal. Calcd for $C_{27}H_{29}O_2P$: C, 77.86; H, 7.02. Found: C, 77.84; H, 7.09.

***trans*-(4-Ethoxy-2-methyl-4-cyclohepten-1-yl)diphenylphosphine oxide (4b)**: 1.48 g (71%); white solid, mp 157.7−158 °C; ^{1}H NMR δ 0.98 (d, J = 7 Hz, 3H), 1.22 (t, J = 7 Hz, 3H), 1.47-2.68 (m, 7H), 3.09 (brd, 1H), 3.57 (q, J = 7 Hz, 2H), 4.51 (brs, 1H), 7.23−7.97 (m, 10H); IR (KBr) 1660 (C=C), 1175 cm^{-1} (P=O); MS m/z 354 (M^+). Anal. Calcd for $C_{22}H_{27}O_2P$: C, 74.55; H, 7.68. Found: C, 74.29; H, 7.69.

***trans*-(4-Ethoxy-2-propyl-4-cyclohepten-1-yl)diphenylphosphine oxide (4c)**: 1.23 g (55%); white solid, mp 124−129 °C; ^{1}H NMR δ 0.58−2.65 (m, 19H), 3.15 (brd, 1H), 3.57 (q, J = 7 Hz, 2H), 4.53 (brs, 1H), 7.26−8.02 (m, 10H); IR (KBr) 1665 (C=C), 1180 cm^{-1} (P=O); MS m/z 382 (M^+). Anal. Calcd for $C_{24}H_{31}O_2P$: C, 75.37; H, 8.17. Found: C, 75.43; H, 8.25.

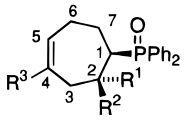
***trans*-(4-Ethoxy-2-isopropyl-4-cyclohepten-1-yl)diphenylphosphine oxide (4d)**: 1.41 g (63%); white solid, mp 149−153 °C; ^{1}H NMR δ 0.75 (d, J = 6 Hz), 0.81 (d, J = 6 Hz) (total 6H), 1.20 (t, J = 7 Hz, 3H), 1.47−2.80 (m, 8H), 3.25 (brd, 1H), 3.56 (q, J = 7 Hz, 2H), 4.55 (brs, 1H), 7.25−8.01 (m, 10H); IR (KBr) 1665 (C=C), 1180 cm^{-1} (P=O); MS m/z 382 (M^+); HRMS calcd for $C_{24}H_{31}O_2P$ 382.2060, found 382.2064.

***trans*-(4-Ethoxy-2,2-dimethyl-4-cyclohepten-1-yl)diphenylphosphine oxide (4e)**: 0.80 g (37%); white solid, mp 134−135 °C; ^{1}H NMR δ 0.94 (s, 3H), 1.16 (s), 1.24(t, J = 7 Hz) (total 6H), 1.60−2.76 (m, 7H), 3.61 (q, J = 7 Hz, 2H), 4.49 (brt, 1H), 7.30−8.00 (m, 10H); IR (KBr) 1660 (C=C), 1180 cm^{-1} (P=O); MS m/z 368 (M^+). Anal. Calcd for $C_{23}H_{29}O_2P$: C, 74.98; H, 7.93. Found: C, 75.03; H, 7.95. (2,2-Dimethyl-4-oxocycloheptyl)diphenylphosphine oxide (**5**), (7-methyl-5-oxo-6-octenyl)diphenylphosphine oxide (**6**), and ethyl diphenylphosphinate (**7**) were also obtained. **5**: 0.13 g (7%); white solid, mp 196−198 °C; ^{1}H NMR δ 1.04 (s), 1.12 (s) (total 6H), 1.32-

(10) Marmor, R. S. *J. Org. Chem.* **1972**, *37*, 2901−2904.

(11) (a) Purdum, W. R.; Berlin, K. D. *J. Org. Chem.* **1975**, *40*, 2801−2806. (b) Marsi, K. L.; Lynch, D. M.; Hormer, G. D. *J. Heterocycl. Chem.* **1972**, *9*, 331−334. (c) Märkl, G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 620.

Table 1. ^{13}C Chemical Shifts (ppm) and $^{13}C-^{31}P$ Coupling Constants (Hz) in Cycloheptenyldiphenylphosphine Oxide Derivatives



R^1	R^2	R^3	product	C_1	C_2	C_3	C_4	C_5	C_6	C_7
Ph	H	EtO	**4a**	42.6 (J_{PC} = 69.6)	41.7	38.4 (J_{PC} = 8.6)	155.3	95.9	25.7 (J_{PC} = 11.6)	24.8 (J_{PC} = 1.8)
Me	H	EtO	**4b**	43.6 (J_{PC} = 69.0)	29.5	36.6 (J_{PC} = 4.9)	155.4	95.7	25.5 (J_{PC} = 13.4)	24.4 (J_{PC} = 1.2)
Pr	H	EtO	**4c**	42.2 (J_{PC} = 69.0)	33.8	37.4 (J_{PC} = 10.4)	155.3	95.7	25.4 (J_{PC} = 13.4)	23.9
i Pr	H	EtO	**4d**	39.2 (J_{PC} = 69.0)	41.0 (J_{PC} = 1.2)	32.1 (J_{PC} = 1.8)	156.4	96.2	*a*	*a*
Me	Me	EtO	**4e**	47.6 (J_{PC} = 68.4)	36.4 (J_{PC} = 1.8)	47.7 (J_{PC} = 11.0)	156.2	93.8	25.6 (J_{PC} = 9.2)	23.9
Ph	H	Ph	**16**[b]	42.6 (J_{PC} = 69.2)	43.7	37.8 (J_{PC} = 9.2)	*a*	*a*	30.6 (J_{PC} = 12.7)	23.9

[a] Not determined. [b] Cited from the previous paper.[1]

2.60 (m, 8H), 3.48 (brd, 1H), 7.35−8.02 (m, 10H); ^{13}C NMR δ 22.1 ($^3J_{PC}$ = 9.2 Hz), 26.1, 29.3 ($^3J_{PC}$ = 3.7 Hz), 30.8 ($^3J_{PC}$ = 6.7 Hz), 36.9 ($^2J_{PC}$ = 1.8 Hz), 43.5, 47.8 ($^1J_{PC}$ = 67.8 Hz), 56.4 ($^3J_{PC}$ = 7.3 Hz), 212.8, and aromatic carbons; IR (KBr) 1695 (C=O), 1180 cm^{-1} (P=O); MS *m*/*z* 340 (M^+). Anal. Calcd for $C_{21}H_{25}O_2P$: C, 74.10; H, 7.40. Found: C, 74.16; H, 7.42. **6**: 0.09g (5%); white solid, mp 87−89 °C; ^1H NMR δ 1.48−1.89 (m), 1.86 (s) (total 7H), 2.00−2.51 (m), 2.11 (s) (total 7H), 6.02 (brs, 1H), 7.30−7.88 (m, 10H); ^{13}C NMR δ 20.7, 21.3 ($^2J_{PC}$ = 3.7 Hz), 25.4 ($^3J_{PC}$ = 15.3 Hz), 27.6, 29.7 ($^1J_{PC}$ = 71.4 Hz), 43.6, 123.7, 155.1, 200.3, and aromatic carbons; IR (KBr) 1685 (C=O), 1185 cm^{-1} (P=O); MS *m*/*z* 340 (M^+); HRMS calcd for $C_{21}H_{25}O_2P$ 340.1590, found 340.1560. **7**: 0.26 g (18%); a colorless oil; ^1H NMR δ 1.37 (t, J = 7 Hz, 3H), 4.11 (dt, J_{PH} = J_{HH} = 7 Hz, 2H), 7.30−7.96 (m, 10H); IR (neat) 1230 cm^{-1} (P=O); MS *m*/*z* 246 (M^+).

Reaction of 2 with Ethyl Benzoate. 1-Phenylcyclopentene (**8**) (0.14 g, 33%) was obtained as a colorless oil from the reaction of phosphonium salt **1** (1.00 g, 2.94 mmol), *t*-BuOK (0.33 g, 2.94 mmol), and ethyl benzoate (0.44 g, 2.93 mmol) under the same reaction conditions as for **2** with enoates. **8**: ^1H NMR δ 1.82−2.19 (m, 2H), 2.37−2.85 (m, 4H), 6.12−6.22 (m, 1H), 7.08−7.52 (m, 5H); ^{13}C NMR δ 23.48, 33.24, 33.37, 125.60, 126.03, 126.81, 128.81, 128.24, 136.90, 142.52; IR (neat) 3090, 3060, 3040, 2960, 2940, 2850, 1600, 1575, 1500, 1450, cm^{-1}; Ms *m*/*z* 144 (M^+); HRMS calcd for $C_{11}H_{12}$ 144.0939, found 144.0965. The fraction consisting of **7** and a trace amount of unidentified compound (0.54 g) and a mixture of **7** and (5-ethoxy-5-phenyl-4-pentenyl)diphenylphosphine oxide (**9**) (0.08 g, ca 4:7 from ^1H NMR) were also separated by flash column chromatography. **9** could not be isolated, but the structure was assigned to **9** on the basis of the ^1H NMR, ^{13}C NMR, and HRMS of the mixture. **9**: ^1H NMR δ 1.21 (t, J = 7 Hz, 3H), 1.57−2.53 (m, 6H), 3.64 (q, J = 7 Hz, 2H), 5.20 (t, J = 7 Hz), 7.19−7.95 (m, overlapped on aromatic protons of $Ph_2P(O)OEt$); ^{13}C NMR δ 15.3, 21.7 ($^2J_{PC}$ = 3.7 Hz), 26.8 ($^3J_{PC}$ = 15.3 Hz), 29.39 ($^1J_{PC}$ = 72.0 Hz), 65.9, 113.3, 154.4, and aromatic carbons; HRMS calcd for $C_{25}H_{27}O_2P$ 390.1747, found 390.1758.

Reaction of 2 with Ethyl Acrylate. The 1:3 adduct **15** of the ylide **2** and ethyl acrylate was isolated as a colorless oil (0.10 g, 37% based on acrylate) from the reaction of **1** (0.50 g, 1.47 mmol), *t*-BuOK (0.17 g, 1.52 mmol), and ethyl acrylate (0.15 g, 1.50 mmol) under the same reaction conditions. **15**: ^1H NMR δ 1.06−2.68 (m, 25H), 3.51 (q, J = 7 Hz, 2H), 3.91−4.20 (m, 4H), 7.31−8.17 (m, 10H); ^{13}C NMR δ 13.22, 13.30, 14.36, 23.7−32.23 (multiple peaks), 41.7 ($^1J_{PC}$ = 67.8 Hz), 59.19, 59.27, 63.33, 120.78, 150.52, 172.44, 172.57 and aromatic carbons; IR (neat) 3075, 2780, 2890, 1735, 1685, 1595, 1445, 1380, 1300, 1265, 1180 cm^{-1}; MS *m*/*z* 540 (M^+); HRMS calcd for $C_{31}H_{41}O_6P$ 540.2638, found 540.2671.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan (No. 06750875). We thank Prof. Dr. R. Iriye and Mrs. Mizuho Hattori for the NMR measurements, and we are grateful to Ihara Chemical Co., Ltd. for the gift of triphenylphosphine.

Supporting Information Available: ^1H and ^{13}C NMR spectra of **4a**−**e**, **5**, **6**, **8**, and **15** and ORTEP diagram of **16** (19 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any masthead page for ordering information.

JO970751S